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EUROPIUM OXALATE ION ASSOCIATION IN WATER

by

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ABSTRACT

The partitioning of radiotracer $Eu^{152/154}$ between aqueous sodium oxalate (Na_2L) solutions and toluene solutions of thenoyltrifluoroacetone (HTTA) has been studied as a function of the oxalate concentration. The pH of the aqueous phase was controlled by means of sodium acetate/acetic acid mixtures and the ionic strength (I) by NaCl or $NaClO_4$.

At low ionic strengths (~ 0.05) and $[L] \sim 10^{-4}$M EuL^+ formed, but at I = 0.95 and $[L] \sim 10^{-3}$M EuL_2^- also formed. Stability constants for the 1:1 and 1:2 (metal:ligand) complexes are reported.

The magnitudes of the stepwise stability constant ratios are discussed.

INTRODUCTION

Rare-earth-oxalate complexing in solution has been studied extensively by Crouthamel and Martin (1) and by Sekine (2). The absolute magnitudes of the stability constants of the complexes cannot be compared

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directly because of the vastly different ionic strengths used in these works. However, the ratios of the stepwise stability constants are clearly at variance (Table I). The stepwise stability constant is defined as

$$[1] \qquad b_n = \left[EuL_n\right] \Big/ \left[EuL_{n-1}\right] \left[L\right] ,$$

where L is the ligand.

Bjerrum (3) has shown that for simple complexes

$$[2] \qquad P = b_1 : b_2 = S \times T \times R,$$

where S is a statistical factor and T is a measure of the work done in bringing a charged ligand from infinity to its equilibrium position in the 1:2 complex against the repulsive force exerted by already bound ligands. For singly-charged ligands that bind to rare-earth or transition metal ions it has been shown that T = 1.6 (4, 5). If the cation has N available sites and if, e.g. the ligand is monodentate S = 2 x N/(N-1), i.e. S > 2. The factor of 2 arises because the probability of a ligand's leaving the 1:2 complex is twice that of a ligand's leaving the 1:1. The R factor, termed the rest effect, covers those contributions to P that are neither statistical nor electrostatic. R will be an important entity in stepwise reactions where, e.g. the cation coordination number changed. Steric hindrance is another obvious contributor to R. The magnitudes of the ratios of the stepwise stability constants are discussed later in this paper.

The solvent extraction-radiotracer technique has proved useful in the study of rare-earth ion association reactions in solution (6). The method is particularly applicable in the present work because of the low

solubility of europium oxalate. In this work $[Eu] \sim 10^{-7}$M and $[\text{oxalate}] \sim 10^{-4}$M.

EXPERIMENTAL

The experimental techniques have been described in detail in earlier publications (7). The organic phase was 0.035 M thenoytrifluoroacetone (HTTA) in toluene. Sodium perchlorate, prepared from $HClO_4$ and NaOH was used to maintain a constant ionic strength, although in some "runs" at low I NaCl was used. The pH was kept constant by means of a 0.0040 M sodium acetate/acetic acid mixture. At low I values the pH was 4.69 and at high I the pH was 5.42. Sodium oxalate and sodium chloride were dried at 110°C prior to use. All reagents were of Analytical Reagent grade, except for HTTA which was recrystallised from hexane. $Eu^{152/154}$ of high specific activity was purchased from the Radiochemical Centre, Amersham, England.

The aqueous and pre-equilibrated organic phases were shaken for three hours in Erlenmeyer flasks fitted with polytetrafluoroethylene (PTFE) sleeves. The phases were separated and assayed for $Eu^{152/154}$ using an annular-type scintillation assembly coupled to an automatic sample changer. At least 20,000 counts were recorded, giving a standard deviation of ±0.7 per cent. The temperature was 25 ±0.5°C.

THEORY

The distribution coefficient is defined as

[3] $$D = [Eu]_o / [Eu]_w,$$

where "o" and "w" designate organic and aqueous species respectively. Distribution coefficients were generally reproducible to ±2%, although when $L = 0$ errors were greater, due possibly to tracer adsorption on the walls of the glass vessels. For this reason, at least two determinations were made of the distribution coefficient at $L = 0$.

When $L = 0$, omitting ionic charges

$$[4] \qquad D^{o} = \frac{\left[Eu(TTA)_3\right]_o}{\left\{[Eu] + [EuA]\right\}_w} ,$$

where A = acetate ion. Only the 1:1 EuA species forms under these experimental conditions (7).

In the presence of oxalate,

$$[5] \qquad D = \frac{\left[Eu(TTA)_3\right]_o}{\left\{[Eu] + [EuA] + [EuL] + [EuL_2] + \text{----}\right\}_w}$$

From Equations 1, 3, 4 and 5 is can be readily shown that (7)

$$[6] \qquad F.\ \left\{(D^{o}/D) - 1\right\} / [L] = b_1 + b_1 b_2 [L] + \text{-------} ,$$

where F is a correction factor for lanthanide-acetate complexing, and F is given by the equation

$$F = 1 + b_1' [A] ,$$

where b_1' is a stability constant for EuA.

Equation 6 shows that a plot of $F.\left\{(D^{o}/D) - 1\right\} / [L]$ against $[L]$ is horizontal if only EuL forms, linear with positive slope if EuL_2 forms, and curved, of ever-increasing curvature, if EuL_3 also forms.

RESULTS

In Table II are listed D and L values for europium oxalate systems at different ionic strngths. Free oxalate concentrations were calculated from the expression

$$[8] \qquad C_L / [L] = 1 + \left\{ H^+ \; f_H \; f_L \; / \; K_{a2} \; f_{HL} \right\} ,$$

where C_L is the total ligand concentration, K_a is the dissociation constant of oxalic acid (8), and f_H and f_L are activity coefficients. A second term involving $K_{a1} \times K_{a2}$ gives an insignificant contribution to $C_L/[L]$. The Davies' form of the Debye-Huckel expression (9) was used to calculate f values, namely,

$$[9] \qquad - \log f = 0.509 . z^2 \left\{ \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3 \; I \right\} ,$$

where z is the ionic charge. The C_L/ L values at different ionic strengths are listed in Table II. Free acetate ion concentrations were estimated from the relationship

$$[10] \qquad C_A / [A] = 1 + [H^+] \; f_H \; f_A \; / \; K'_a ,$$

where K′a is the dissociation constant of acetic acid (= ~ 1.74×10^{-5}, ref. 10).

To calculate F at low ionic strengths, b_1 values were evaluated by adjusting the b'_1 value of Kolat and Powell (10) at I = 0.1 to the relevant I using Equation 9. The applicability of Equations 8 and 9 to the present work has been discussed in an earlier publication (6).

Plots of $F \left\{ D^\circ/D - 1 \right\} / [L]$ against [L] were horizontal at

the lower ionic strengths, indicating that EuL only formed. It follows from Equation 6 that, when $b_2 = 0$, $1/D \propto [L]$. The best straight line of a $1/D$ against $[L]$ plot was determined by the method of least squares. This method gave D^o and also D at a given $[L]$, and b_1 values were calculated by direct substitution of the parameters in Equation 6. The b_1 values determined at different ionic strengths are listed in Table III, together with the thermodynamic b_1 value estimated using Davies' activity expression (9).

The thermodynamic b_1 value $= 3.3 \times 10^6$ for europium oxalate (this work) may be compared with the b_1 values for Ce, Nd, and Yb oxalates of 3.3×10^6, 16×10^6, and 20×10^6 respectively, these values being those determined by Crouthamel and Martin (1). Europium lies between Nd and Yb in the rare-earth series, so that agreement between our work and the solubility work of Crouthamel and Martin is poor. Thermodynamic b_1 values have also been reported (12, 13) for Er oxalate (6.6×10^4) and Y oxalate (3.3×10^6), and this lack of agreement is characteristic of published b_1 values for these oxalate systems. Thus for Ce oxalate, solubility measurements at $I = 2$ (14) give $b_1 = 1.1 \times 10^6$, while ion exchange measurements at $I = 1$ (15) give $b_1 = 1.1 \times 10^4$. A stability difference of two orders of magnitude seems impossibly large to be attributed to activity coefficients. However, our b_1 value for europium oxalate is in good agreement with that estimated for Y (3.3×10^6) by Feibush and co-workers from solubility measurements (13).

Our solvent extraction results at $I = 0.95$ show that $EuC_2O_4^+$ and $Eu(C_2O_4)_2^-$ are formed, and b_1 and b_1b_2 values were estimated from the

intercept and slope of a plot of the L.H.S. of Equation 6 against $[L]$. The b_1 and b_2 values are listed in Table III. The b_1 value for EuA^{2+} has not been reported at I = 1 or I = 2, and Sonesson's b_1 value (16) for SmA^{2+} at I = 2 has been used. The F values were calculated, therefore, on the basis that b_1 = 100. The $C_L / [L]$ correction is small (3%), so that the calculation of activity coefficients at I = 0.95 using the Davies' equation (9) should not introduce too great an error. The estimated error in the quoted stability constants is probably less than 20%. Our b_1 value (= 1.15×10^5) is not in accord with the results of Sekine ($b_1 = 6 \times 10^4$, ref. 2).

The b_1:b_2 ratios are of interest, however. Our b_1:b_2 value at I = 0.95 is in reasonable agreement with the values estimated by Crouthamel and Martin (Tables I and III). A sampling of the P values, listed in the Chemical Society tabulations of stability constants (17), for transition metal oxalates shows that P ~ 250. Consequently, P values ~ 250 would seem to be correct for rare-earth and transition metal oxalates.

In an earlier publication it was shown that a T value = 1.6 explained the magnitudes of P values for rare-earth and transition metal complexes with some α-hydroxymonocarboxylates (4). This T value was also valid for some Zn and Ni halide complexes (5). The T factor was independent of the nature of the (singly-charged) ligand, and this was part of the evidence put forward to show that the factor of 1.6 was of mainly electrostatic character. N. Bjerrum (18) has shown that

$$\log T = \frac{1}{2.303} \times \frac{e^2}{D_c r} \times \frac{1}{k.K} \quad ,$$

where e is the ligand charge, r the equilibrium separation of the ligands, D_c the dielectric constant, k the Boltzmann constant and K the absolute temperature. Assuming that r(oxalate)~r (α-hydroxymonocarboxylate), log T(oxalate) = 4 log T (α-hydroxymonocarboxylate), or T(oxalate) = $1.6^4 \sim 6.5$. Hence, for 6-coordinated metal ions, P(calc.) = 4.8 x 6.5~30, while for 8-coordinated ions, P(calc.) = 3.5 x 6.5~25. These P(calc.) values are almost an order of magnitude smaller than the P(obs.) values determined in this investigation and by Crouthamel and Martin (1). This is also the case with the transition metal oxalates. Sekine's (2) results are indicative of a large stabilising effect in the second association stage. However, our P values are in agreement with those determined by Crouthamel and Martin (1) and also those measured for a number of transition metal oxalates, and it would seem that Sekine's values are incorrect. Sekine's (2) results would indicate that R ~ 0.25, and it is difficult to postulate a mechanism that preferentially aids the second associate stage. Such reactions as the disruption of the cation hydration sheath on changes in metal-oxalate bond length would be expected to confer increased stability on the 1:1 complex. It would seem, therefore, that rest effects are present in these rare-earth and transition metal oxalate systems. J. Bjerrum (3) defined the rest effect as the influence of bound ligands on the binding power of the metal ion. Steric effects are negligible in these systems. It is possible that the strength of the metal-ligand bond is different in the first and second stages of ion association. This effect would be due to a lengthening of the M– L bond length in the 1:2 complex, and, in the extreme

case, one can imagine the M–L bonding changing from low covalent character in the 1:1 complex to purely electrostatic character in the 1:2 complex.

CONCLUSION

Stepwise stability constants have been determined for europium-oxalate complexes in water. The solvent extraction -radiotracer technique was employed. The magnitudes of the ratios of stepwise stability constants suggest that the 1:2 complexes are weaker than expected from statistical and electrostatic considerations. The suggestion is made that the M – L bond length is greater in the 1:2 complex than the 1:1.

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PGM:vn

Table I. Stability constant ratios for oxalate complexes

Crouthamel and Martin		Sekine	
Ce	360	La	4.7
Nd	800	Eu	6.6
Yb	500	Lu	11

Table II. $[L]$, F and 100/D values for Eu-oxalate

I = 0.027		I = 0.036		I = 0.052		I = 0.054		I = 0.061		I = 0.95	
$C_L/[L] = 1.176$		$C_L/[L] = 1.167$		$C_L/[L] = 1.155$		$C_L/[L] = 1.153$		$C_L/[L] = 1.149$		$C_L/[L] = 1.031$	
F = 1.696		F = 1.63		F = 1.54		F = 1.53		F = 1.50		F = 1.34	
10^5 L	100/D	10^5 L	100/D	10^5 L	100/D	10^5 L	100/D	10^5 L	100/D	10^4 L	100/D
0	1.73	0	2.63	0	2.81	0	2.89	0	8.92	0	0.147
0.680	5.47	0.917	6.10	1.385	8.99	1.39	10.86	1.39	34.0	3.88	4.90
0.850	7.20	1.145	8.02	1.73	10.61	1.735	12.28	1.74	37.55	7.77	11.60
1.70	11.50	2.29	14.31	3.46	17.42	3.47	19.71	3.48	66.35	9.70	19.4
2.55	15.88	3.43	17.60	5.19	22.96	5.20	39.04	5.22	87.3	19.4	57.9
3.40	23.39	4.57	26.72	6.93	37.41	6.94	47.9	6.96	113.1	29.1	93.6
4.25	26.98	5.72	31.91	8.66	43.10	8.67	49.0	8.70	136.8	38.8	122.1

Table III. Stability constant for Eu-C_2O_4 complexes

I	0.027	0.036	0.052	0.054	0.061	0.95
10^{-5} b_1	5.95	4.50	2.70	3.10	2.05	1.15
10^{-2} b_2						4.6
$b_1:b_2$						250
10^{-6} b_1 (thermo)	3.85	3.60	2.95	3.55	2.55	

Average b_1 (thermodynamic) = 3.3 ($\pm$0.5) x 10^6